# Transient Attenuated Total Internal Reflection Spectroscopy to Measure the Relaxation Kinetics of Triplet State of Tetra(*N*-methylpyridinium-4-yl)porphine at Liquid-Liquid Interface

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Tetra(*N*-methylpyridinium-4-yl)porphine (tmpyp$^{4+}$) was adsorbed to the toluene/water interface with dodecylsulfate ions. Transient attenuated total internal reflection spectroscopy was developed to measure the relaxation kinetics of the triplet state of tmpyp$^{4+}$ generated by laser irradiation at the interface. For both a probe white light and a pulsed 532 nm-laser light, the angle of incidence was set to 67° that was larger than the critical angle at the interface, 63°. It was observed that the triplet tmpyp$^{4+}$ at the interface was quenched faster than in aqueous solutions.

Total internal reflection (TIR) spectroscopy is one of the effective methods to obtain the information of a solute at the liquid-liquid interface and near the interface directly. We have investigated the interfacial adsorption equilibria of Rhodamine B derivatives[1] and porphyrins[2,3] by total internal reflection fluorometry (TIRF). Recently, time-resolved TIRF is applied to measure the lifetime of a solute or the rotational dynamics of a solute at the interface,[4] but there are no reports on the direct observation of chemical reactions at the liquid-liquid interface so far. Time-resolved total internal reflection spectroscopy has a high potential to measure fast chemical reactions at the liquid-liquid interface, which are hard to be investigated by other techniques.

Normally organic phase has a higher refractive index than aqueous phase in a two-phase system. Therefore, when a light was irradiated to an interface through an organic phase at an angle of incidence of larger than the critical angle ($\theta_c$), the total internal reflection occurs at the interface, *i.e.*, unity reflectance ($R$). When a light-absorbable solute is adsorbed to the interface, $R$ is less than 1, *i.e.*, an attenuated total internal reflection (ATR) condition. For the ATR, the reflection absorbance of a solute ($A_R$) at the interface is defined[5] as $-\log R$. When a transparent organic phase is used, $A_R$ can be simply expressed as:[5]

$$A_R = \varepsilon_i b_i c_i + \varepsilon_a b_a c_a \qquad (1),$$

where $\varepsilon$ is the molar absorption coefficient of a solute, $b$ is the effective thickness, and $c$ is the concentration of the solute. Subscripts i and a imply the interface and aqueous phase, respectively. Both $b_i$ and $b_a$ are complicated functions of refractive indices of organic, aqueous and interfacial phases, the angle of incidence, and the electric field strength in these phases; $b_i$ and $b_a$ are also functions of the thickness of the interfacial phase ($h$) and the penetration depth ($d_p$), respectively.

When the first term of the right-hand side in eq 1 is much larger than the second term, $A_R$ is proportional to $c_i$. Under this condition, a transient attenuated total internal reflection (TATR) spectrum corresponds to the transient absorption spectrum (TAS) of the interfacial species. In the present study, we will propose the TATR spectroscopy for the first time and show experimental results of relaxation kinetics for the triplet state of a porphyrin generated by laser excitation.

We examined the adsorption equilibrium of 5,10,15,20-tetra(*N*-methylpyridinium-4-yl)porphine (tmpyp$^{4+}$) to the toluene/water interface together with hexadecylsulfate ion by means of the TIRF in the previous paper.[2] In this study, dodecylsulfate ion was used instead of hexadecylsulfate ion, because of its higher purity. Aqueous phase contained $1.0\times10^{-6}$ M (1 M = 1 mol·dm$^{-3}$) tmpyp$^{4+}$, $1.05\times10^{-5}$ M sodium dodecylsulfate (purity ≥ 98%), $5.0\times10^{-4}$ M acetate buffer and 0.10 M NaCl. pH was adjusted to 4.3. 0.70 cm$^3$ of the aqueous phase was taken to a 1.0 cm quartz cell whose upper part was treated with dimethyldichlorosilane to generate a flat interface,[1–3] and then 0.70 cm$^3$ of toluene phase was carefully added not to disturb the flat interface. A small magnetic stirrer was mildly stirred at 7.2 rpm in the aqueous phase. All experiments were done at 25±1 °C.

As for ATR measurements, a continuous white light from a 150 W xenon lamp was irradiated through the toluene phase to the interface at an angle of incidence 67° that was larger than the $\theta_c$ at the toluene/water interface, 63°. ATR spectra were measured as a function of adsorption time (0–120 min) with a gated image intensifier (C2925-01, Hamamatsu Photonics) attached to a polychromator and a detection system (TSP-601, Unisoku, Osaka, Japan). As for TATR, pulsed 532 nm-laser lights were also irradiated at an angle of incidence 67° with polarization parallel to the plane of incidence (*p*-polarized),[6] and they crossed to the probe white light at the right angle (see Figure 1). Laser photolysis was done with an Nd:YAG laser (Surelite I-10, 10 Hz, Continuum) equipped with a second harmonic generator and the detection system. The laser pulse width and power were about 6 ns and 15–19 mJ/pulse, respectively. The intensity of the probe light reflecting at the interface was measured by a photomultiplier attached to a monochromator. The output of the photomultiplier was connected to a digital oscilloscope (TDS-320, SONY Tektronix), which was triggered by a split laser light. Transients obtained by 200 laser shots were averaged for each measurement. The time constant ($\tau$) for the decay of a transient species was obtained by applying the non-linear least-

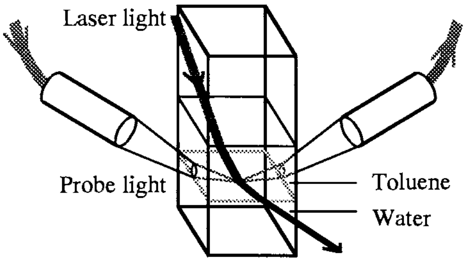

**Figure 1.** An apparatus to measure the transient attenuated total internal reflection spectra of tmpyp$^{4+}$ adsorbed to the toluene/water interface. For both a probe white light and a pulsed 532 nm-laser light, the angle of incidence was set to 67°.

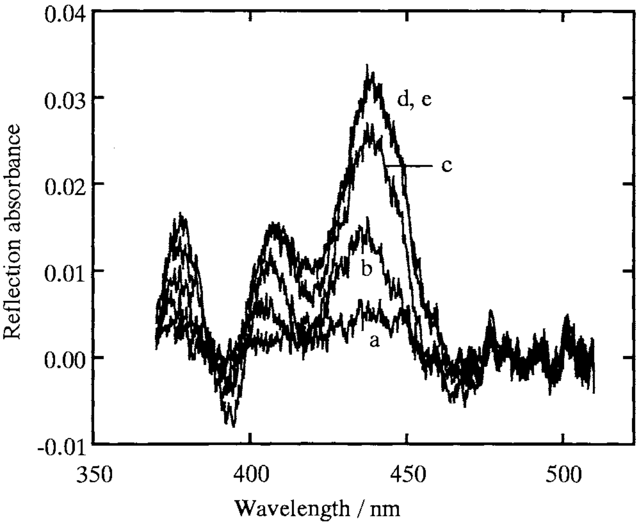

**Figure 2**. The ATR spectra of tmpyp$^{4+}$ adsorbed to the toluene/water interface. After (a), 5 min; (b), 17 min; (c), 37 min; (d), 48 min; (e), 74 min.

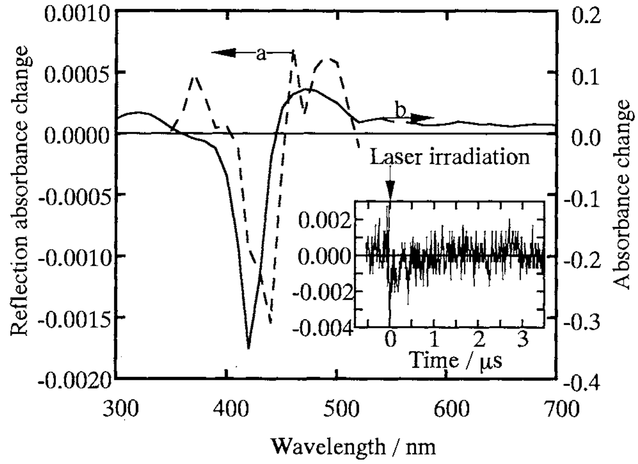

**Figure 3**. (a) The TATR spectrum of tmpyp$^{4+}$ adsorbed to the toluene/water interface. Laser power, 19 mJ/pulse; 200 laser shots and 0.05–0.20 μs were averaged. The inserted figure represents the time profile at 430 nm. (b) The TAS of tmpyp$^{4+}$ at 0.50 μs in an aqueous solution. tmpyp$^{4+}$, $1.0\times10^{-6}$ M; acetate, $5.0\times10^{-4}$ M; NaCl, 0.1 M; pH, 4.68; laser power, 15 mJ/pulse; 50 laser shots were averaged.

squares method to the reflection absorbance change at a single wavelength after laser irradiation. The transients were measured over the wavelength range 350–520 nm in 10 nm steps.

Figure 2 shows the change of ATR spectra of tmpyp$^{4+}$ at the interface. By this method, the observed ranges for the interface and for the aqueous phase are $h$ and $d_p$, respectively. We postulate from the molecular dynamics simulation that the $h$ is about a few nm, whereas we calculated the $d_p$ to be 89 nm. If tmpyp$^{4+}$ is not adsorbed to the interface, all tmpyp$^{4+}$ remain in the aqueous phase. Under this condition, the $\varepsilon_a\, b_a\, c_a$ term in eq 1 is estimated to be less than $2\times10^{-5}$ at 422 nm ($\varepsilon_a$=$2.2\times10^{5}$ M$^{-1}$ cm$^{-1}$), which is much less than the observed $A_R$ values. This implies that the $A_R$ included only the absorption by the tmpyp$^{4+}$ adsorbed to the interface, *i.e.*, $A_R \approx \varepsilon_i\, b_i\, c_i$. The Soret band of tmpyp$^{4+}$ at about 438 nm increased with time in Figure 2, and reached the adsorption equilibrium at 50 min. The Soret band is 422 nm in aqueous solutions, and this suggests the ionic interaction between tmpyp$^{4+}$ and dodecylsulfate ions and/or aggregation at the interface. This spectral shift was also observed in the previous study of TIRF,[2] in which the excitation spectrum of tmpyp$^{4+}$ at the interface was shifted to 433 nm at the hexadecylsulfate concentration of $1.05\times10^{-5}$ M.

After the adsorption equilibrium was attained, the laser photolysis was done. Figure 3 shows the TATR spectrum as well as TAS of tmpyp$^{4+}$ in an aqueous solution. Since both spectra well agreed with each other, the same transient species was generated both at the interface and in the aqueous solutions. Triplet state of tmpyp$^{4+}$ was known to be generated in aqueous solutions by the 347 nm-laser irradiation,[7] and its TAS is quite similar to ones obtained in this study. These facts meant that the transient species of tmpyp$^{4+}$ generated at the interface by the 532 nm-laser photolysis was triplet state of tmpyp$^{4+}$. The intensity of probe light changed for all wavelengths at the moment of the laser irradiation, suggesting that the thermal lens effect was relaxed very fast ($\tau \le 50$ ns).

The $\tau$ value of the triplet tmpyp$^{4+}$ was 1.84±0.02 μs (n=7) in aqueous solutions under aerated conditions, whereas that is 0.72±0.12 μs (n=4) at the interface. The faster decay rate at the interface suggests that the triplet-triplet annihilation or energy transfer occurs at the interface because of the high interfacial concentration of tmpyp$^{4+}$. This was supported by the red-shift of the Soret band at the interface, mentioned above. Detailed studies of the quenching mechanism at the interface are now in progress. In conclusion, the decay kinetics of the triplet state of a porphyrin was measured by TATR for the first time and the decay rate at the interface was found to be faster than in the aqueous phase.

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